The University of Chicago

# I. Colors of the Second Order
# II. Mercuri-Organic Derivatives

## A DISSERTATION

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BY

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## A DISSERTATION

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# NITROSO-TRIPHENYLAMINE AND COLORS OF THE SECOND ORDER[1]

It is a well-known rule[2] that the color of a yellow dye changes with increase of molecular weight to orange, red, violet, blue, and finally to green. Each one of these colors is called lower than the preceding one, and higher than the following one. Generally, we can lower the color by the introduction of alkyl or aryl radicles into the auxochromic or chromophoric groups of the dye.

The spectroscopic explanation of this behavior of dyes is that a yellow dye has an absorption band in the violet, and any increase in the molecular weight decreases the number of vibrations corresponding to this absorption band causing the band to shift toward the red end of the spectrum. When the absorption band is in the blue the compound appears orange, and as the absorption band goes through green, yellow, orange to red, the color of the respective compounds successively changes to red, violet, blue, and green. A compound has the color complementary to that of its maximum absorption. On the other hand, if in the molecule of a yellow dye we make such changes as generally tend to produce a higher color, then the absorption bands shift into the ultra-violet part of the spectrum, the compound becoming colorless.

Absorption colors have very much in common with interference colors. The colors of Newton, for instance, are also produced by an absorption band going through the spectrum in the same direction in which the absorption bands of chemical compounds shift with increase of molecular weight. Thin layers of any oil, soap bubbles and glass are first yellow in reflected light, and as the thickness of the layer increases, the color becomes orange, red, violet, blue and green. The last color has an absorption band in the red, but in the violet end of the spectrum there appears a new band. If the layer becomes still thicker, the first band (in the red) shifts into the ultra-red, and we have only the second band, which is in the violet. Our layer is now again yellow but yellow of the second order.
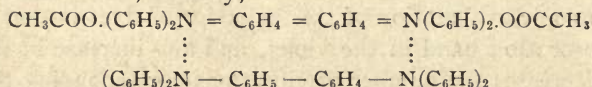
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[1] This work was carried out in co-operation with Professor J. F. Piccard and published in *J. Am. Chem. Soc.*, **40**, 1074 (1918), in an article by J. F. Piccard and M. S. Kharasch.

[2] Nietzki, *Verh. des Vereins zur Förderung des Gewerbefleisses*, **58**, 231 (1879).

Some years ago Professor Piccard became interested in what would happen if a dye with a lower color than green were prepared. This problem was undertaken by me in collaboration with Professor Piccard. The number of green dyes is relatively small, and most of them have already so many alkyl and aryl radicles in their auxochrome and chromophore groups that any further increase in molecular weight is almost impossible. In the field of meriquinoid dyes an opportunity for such experiments was found. These dyes begin with yellow (meriquinone di-immonium salts)

$$ClNH_2 = C_6H_4 = NH_2Cl$$
$$\vdots \qquad\qquad \vdots$$
$$NH_2 — C_6H_4 — NH_2$$
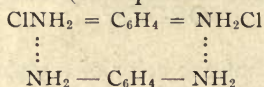
and go to green (meri-tetramethyl-diphenoquinone-di-immonium salt). When we substituted 8 phenyl groups for the 8 methyls in the last named green compound, a substitution which always lowers the color, a new yellow dye was obtained which was the first representative of absorption colors of second order, namely,

$$CH_3COO.(C_6H_5)_2N = C_6H_4 = C_6H_4 = N(C_6H_5)_2.OOCCH_3$$
$$\vdots \qquad\qquad\qquad\qquad \vdots$$
$$(C_6H_5)_2N — C_6H_5 — C_6H_4 — N(C_6H_5)_2$$

meri-tetraphenyl-diphenoquinone-di-immonium acetate.

The above mentioned experiments demonstrate that the rule for interference colors of second order holds good in case of absorption colors. The first absorption band, or group of absorption bands, is always followed by a second one which corresponds approximately to double the number of vibrations of the first one; it is the octave of the first.

Since the paper of Piccard[1] was published, attention has been called to a few more examples of colors of the second order, but none of them gives a much lower color than yellowish green, or greenish yellow. The new theory led, however, to such encouraging results, in explaining the colors of new compounds, that we have tried to go one step further to prepare an orange compound of the second order. We have chosen the group of p-nitrosoanilines for this work.

In the p-nitrosoanilines the dimethyl compound is already yellowish green. The monophenyl (p-nitroso-diphenylamine) is greenish yellow in benzene solution, while in alcohol it is orange.[2]

$$CH_3NCH_3 \qquad\qquad\qquad\qquad HNC_6H_5$$

Green.      Greenish yellow.

$$NO \qquad\qquad\qquad\qquad NO$$
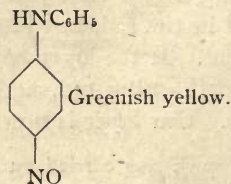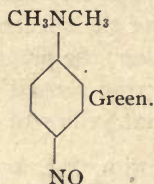
[1] Jean Piccard, *Ber.*, **46**, 1843 (1913).

[2] There is very little doubt as to the fact that the alcoholic solution of the p-nitroso-diphenylamine contains an addition compound. See F. Strauss and Zeime, *Ber.*, **46**, 2267 (1913).

To complete the above given group of dyes, and to compare their colors, it was necessary to have the diphenyl-nitrosoaniline (nitroso-triphenyl-amine). We were puzzled by the fact that nitroso-triphenylamine, which is very interesting from a purely chemical point of view, had not as yet been prepared, and it was not without apprehension that we began this work. In the literature we found mention of several vain attempts to prepare this compound. It seemed, from all the work done, as if in tri-phenylamine the nitrogen had lost all influence on the rest of the mole-cule, the $p$-hydrogen atoms behaving like the hydrogen in benzene. The nitro compound is easily formed, but nitrous acid does not give a nitroso derivative. If any action took place at all, the only isolated product of the reaction was the $p$-nitro-triphenylamine. On the other hand, we know from the work of Wieland that triphenylamine gives on oxidation derivatives of tetraphenylbenzidine.

After experimenting for some time and obtaining only the previously mentioned derivatives, we finally succeeded in working out a method for the preparation of nitroso-triphenylamine. While working out this method, we were influenced by the following considerations. In the well-known Fisher-Hepp reaction, the parahydrogen changes place with the —NO of the nitrosamine group.

$$C_6H_5 - N - C_6H_4 - H \qquad\qquad C_6H_5 - N - C_6H_4 - NO$$
$$\quad\qquad | \qquad\qquad\qquad\longrightarrow \qquad\qquad |$$
$$\quad\qquad NO \qquad\qquad\qquad\qquad\qquad\qquad H$$

We thought that it might not be essential that the —NO group should be in the same molecule as the hydrogen, so we tried to duplicate the con-ditions of the Fisher-Hepp reaction as well as we could, except that the —NO group was attached to another molecule, by using amyl nitrite.

$$(C_6H_5)_2N - C_6H_4 - H + C_5H_{11}O - NO \longrightarrow$$
$$(C_6H_5)_2N - C_6H_4 - NO + C_5H_{11}O - H.$$
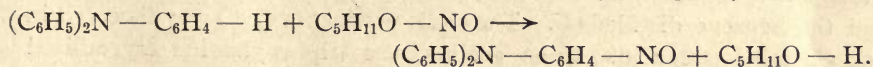
Experimentally this was carried out by treating a suspension of triphenyl-amine in absolute alcohol, saturated with hydrogen chloride, with amyl-nitrite at —5°. In this way we obtained the nitroso compound, the yield being nearly quantitative with respect both to the triphenylamine and the amylnitrite.

The new compound was to our surprise a chloride which could easily be recrystallized from methyl alcohol. The chloride is without doubt $Cl(C_6H_5)_2N : C_6H_4 : NOH$ (diphenyl-quinone-monimine-oxime chloride)[1] triphenylamine having no affinity for HCl.

Nitroso-triphenylamine was easily prepared by the hydrolysis of this salt with water.

The color of the base and the chloride are alike, but we must not forget

[1] We shall use the abbreviation nitroso-triphenylamine hydrochloride hereafter in referring to this compound.

that the former is orange of the second order, and the latter orange of the first order. The colors of the chlorides of nitroso-anilines begin with light yellow, and are very slightly lowered by the introduction of methyl groups. Even the monophenyl derivative is only orange-yellow, so we could not expect a much lower color than orange-yellow for a diphenyl derivative.

On the other hand the color of the free bases begins with green and goes to greenish yellow (nitroso-diphenylamine). For the next member we must expect a still lower color.

The nitroso group of the nitroso-triphenylamine is in the para position. This was proved by reducing the nitroso-triphenylamine with zinc and acetic acid to the amino compound. This in turn was converted with acetyl chloride into the acetyl derivative, which was found to be identical with that prepared by Herz from p-nitrotriphenylamine.[1]

## Experimental Part.

**The Preparation of Triphenylamine.**—The following modified method of Irma Goldberg and Marie Nimerovsky[2] for preparing triphenylamine gave very satisfactory results: A mixture of 116 g. of diphenylamine, 140 g. of phenyliodide, 72 g. of potassium carbonate (1.5 times the theoretical quantity), 2.5 g. of catalytic copper[3] and 300 cc. of nitrobenzene was heated for 12 hours at 207°[4] in a copper flask, fitted with an air condenser. The brown-colored solution was then subjected to steam distillation, whereby the nitrobenzene and the excess of phenyliodide were separated from the products of the reaction. Benzene was added to the mixture of di- and triphenylamines, potassium iodide and copper and the whole filtered through glass wool, to free it from copper. The benzene solution was then separated from the water, dried with anhydrous sodium sulfate, and the benzene distilled off. The crude product (157 g.) was dissolved in hot glacial acetic acid. Upon cooling, the triphenylamine crystallized out (120 g., m. p. 124.5°). When recrystallized from methyl alcohol the triphenylamine was obtained in small, almost colorless crystals, melting at 127°.

**Nitroso-triphenylamine Hydrochloride.**—Twenty g. of triphenylamine was dissolved in 170 cc. of hot absolute alcohol, the solution cooled rapidly and the resulting suspension treated with 300 cc. of a solution of alcohol saturated with hydrogen chloride. Dry hydrogen chloride was then passed through the suspension, and amyl nitrite slowly added, the whole being well cooled (—5°) and constantly shaken during the operation. The solution first turned blue, and, as more amyl nitrite was added, red. The end of the reaction was ascertained by diluting a drop of the solution with

[1] *J. Am. Chem. Soc.*, **39**, 2006 (1917); also *Ber.*, **40**, 2451 (1907).

[2] *Ber.*, **40**, 2451 (1907).

[3] *J. Am. Chem. Soc.*, **39**, 2006 (1917).

[4] The temperature is that of the oil bath in which the copper flask was immersed.

water and testing with potassium iodide-starch paper. The solution was allowed to stand for 2 hours longer at —20°, while a slow stream of dry hydrogen chloride was passed through it. An orange-red to carmine product separated out, the color depending on the quantity of hydrogen chloride introduced. This, the hydrochloride of nitroso-triphenylamine, was filtered off and washed with absolute alcohol. The yield is very good (20 g.).

It is important to note that sometimes smaller or greater quantities of the nitrotriphenylamine are formed along with the nitroso compound, this depending entirely on the quality of the amyl nitrite used. For purification the nitrosotriphenylamine hydrochloride thus obtained was first converted into the free base, by suspending the hydrochloride in cold water for 2 hours. It was then filtered, washed with cold water until a sample of the washings gave no precipitate with silver nitrate, and dried in a vacuum desiccator. When absolutely dry, the free base was dissolved in ether (dried over calcium chloride) and its hydrochloride precipitated by dry hydrogen chloride. The nitrotriphenylamine remained in solution. The hydrochloride when recrystallized[1] from ethyl alcohol (1 g. in 30 cc.) was obtained in long, brown needles melting at 178°.

The chlorine was determined by addition of $AgNO_3$ to the water extract of the hydrochloride.

Subst., 0.5000; AgCl, 0.2283.
Calc. for $C_{18}H_{15}N_2OCl$: Cl, 11.42. Found: 11.30.

*p*-**Nitroso-triphenylamine.**—The free base, obtained by hydrolysis of the pure hydrochloride, was recrystallized twice from methyl alcohol, giving beautiful, long, brown needles, melting at 120.5° (corr.). The powdered substance is orange.

Subst., 0.1268, 0.1012; $CO_2$, 0.3660, 0.2923; $H_2O$, 0.0602, 0.0473, 0.2295, 0.1327; 21.20, 12.40 cc. dry $N_2$ at 20°, 24° and 735.5, 735.5 mm.
Calc. for $C_{18}H_{14}N_2O$: C, 78.83; H, 5.15; N, 10.27. Found: C, 78.70, 78.76; H, 5.27, 5.19; N, 10.42, 10.40.

The nitroso-triphenylamine is soluble in methyl alcohol (1 g. per 30 cc. of the boiling alcohol), more so in ethyl alcohol, and very easily in ether and benzene. In an excess of dil. sulfuric or hydrochloric acid the nitroso-triphenylamine dissolves with a red color, and is not precipitated by the addition of water. An acetic acid solution of the base has the color of bromine.

### Summary.

1. It is possible—under certain conditions—to introduce a nitroso group into the molecule of triphenylamine.

2. The nitroso-triphenylamine so formed is a para compound.

3. The color of *p*-nitroso-triphenylamine is orange of the second order.

[1] The yield was better if after cooling it at —20° we introduced dry HCl gas into the solution.

The following table shows the colors of the different $p$-nitroso-anilines:

| Formula. | Salt. | Base. | Color. In ben-zene sol. | In alco-hol sol. | In alcohol water sol. |
|---|---|---|---|---|---|
| $C_6H_5.NO$[1] | yellow | blue-green (melted) | blue-green | blue-green | . . . |
| $H_2N.C_6H_4.NO$ | yellow | yellowish green | . . . . . [2] | . . . . | . . . . |
| $(CH_3)_2N.C_6H_4.NO$ | yellow | yellowish green | yellowish green | greenish yellow | yellow |
| $(C_6H_5)HNC_6H_4.NO$ | orange-brown | orange | greenish yellow | yellowish orange | orange |
| $(C_6H_5)_2.N.C_6H_4.NO$ | orange-brown | orange | yellow | orange | orange-red |

[1] We indicate here the color of nitroso-benzene, although, strictly speaking, it does not belong to the same family.

[2] We do not know why this mother-substance is much less soluble than the other members of the group. It is probably in connection with this phenomenon that the solutions of this compound are more yellowish than those of the dimethyl derivatives.

## AROMATIC MERCURI-ORGANIC DERIVATIVES.[1]

During the course of investigation of mercuri-organic derivatives undertaken for the Sprague Memorial Institute, the amount of data has accumulated to such an extent that it has been deemed advisable to publish some of the results thus far obtained. This paper contains some preliminary work on the preparation of a 6-membered atomic heterocyclic compound which contains a metal in place of a non-metal. In this case mercury was the metal experimented with. It was put in place of nitrogen in a ring of the azine type. Work is now being carried on to substitute mercury for oxygen, sulfur, and nitrogen, in the type of rings illustrated below.

R—C—Cl ... O          H—N ... S ... $X_2N$ — $NX_2$          $X_2N$ ... O ... N—H ... $NX_2$
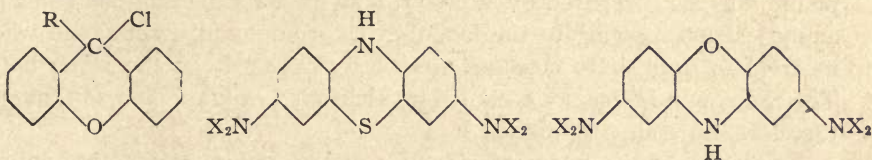
A detailed study of the influence of different groups on the position taken by mercury when introduced into a substituted benzene nucleus is also under investigation.

The theory of mercurization will be published at a later date.

### Experimental.

**The Preparation of *m*-Bromo-dimethyl-aniline,** $m\text{-}BrC_6H_4N(CH_3)_2$.— This compound was first prepared by Wurster,[2] by treating *m*-bromo-aniline with methyl iodide in a sealed tube. The method has the disadvantage that large quantities of *m*-bromo-dimethyl-aniline cannot be made in a single operation. Since we were not interested in obtaining pure *m*-bromo-dimethyl-aniline as such, but a pure *p*-nitroso-*m*-bromo-dimethyl-aniline, the following method was adopted. A quantity of *m*-bromo-aniline (75 g.) was suspended in water (900 cc.) and heated to about 80°. Sodium carbonate (300 g.) and dimethyl sulfate (300 g.) were then added in small portions, care being taken that the solution was always alkaline. The addition should take about 1.5 hours. After all of the dimethyl sulfate had been added, the solution was agitated for an hour and then subjected to steam distillation. The oil which came over was separated

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[1] The material presented here was published in the *J. Am. Chem. Soc.*, **42**, 1855 (1920) in an article by M. Kharasch and J. F. Piccard.

[2] Wurster, *Ber.*, **12**, 1818 (1879).

from the distillate, the latter extracted twice with ether, and the portions combined. The ether solution was dried with sodium sulfate, the ether distilled off, and the oil distilled *in vacuo*. A colorless oil came over which, however, turned yellow on standing. Yield, 75 g.

The product thus obtained contains unchanged *m*-bromo-aniline, *m*-bromo-monomethyl-aniline and *m*-bromo-dimethyl-aniline. To separate these 3 substances, the usual method was employed. The oil was dissolved in 2.5 mols. of 20% hydrochloric acid, the solution cooled to 0°, and the calculated amount of sodium nitrite[1] dissolved in a little water was added in small amounts. The hydrochloride of the *p*-nitroso-*m*-bromo-dimethyl-aniline separated. The solution was then extracted repeatedly with ether until a sample test showed the absence of *m*-bromo-phenyl-methyl-nitrosamine in the latter.[2] The precipitate—the hydrochloride of the *p*-nitroso-*m*-bromo-dimethyl-aniline—was then filtered off and dried in a vacuum desiccator.

**$p$-Nitroso-$m$-bromo-dimethyl-aniline,** $(CH_3)_2NC_6H_3BrNO$.—This compound was also prepared by Wurster, who gave its melting-point but no analytical data, owing to the fact that the compound decomposed when he tried to bring it to constant weight by drying it on the water-bath. The compound is also not recorded in Richter's Lexikon. It was thought, therefore, advisable to analyze it.

A quantity of the hydrochloride of *p*-nitroso-*m*-bromo-dimethyl-aniline (5 g.) was suspended in 75 cc. of water, cooled to 0°, 40 cc. of ether added, and enough carbonate to render the solution decidedly alkaline. The ether extract was then separated from the solution, and the latter extracted 3 more times with ether, 50 cc. being used each time. The ether extracts were combined, dried with sodium sulfate, and $^3/_4$ of the ether distilled off. The solution was then transferred to an evaporating dish and allowed to evaporate spontaneously. Beautiful long green needles were obtained which melted with decomposition at 148°.[3] For analysis the base was recrystallized twice from very small amounts of ether.

Subs., 0.1082: AgBr, 0.0886.
Calc. for $C_8H_{11}ON_2Br$: Br, 34.87. Found: 34.84.

**$m$ - Bromo - dimethyl - $p$ - phenylene - diamine Dihydrochloride,** $BrNH_2C_6H_3N(CH_3)_2.2HCl$.—The hydrochloride of *p*-nitroso-*m*-bromo-dimethyl-aniline was reduced in the following manner. Twice the calculated amount of stannous chloride necessary for the reduction was dissolved in conc. hydrochloric acid, the solution diluted somewhat, warmed to 40°, and the *p*-nitroso-*m*-bromo-dimethyl-aniline hydrochloride, mixed

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[1] To avoid an excess of sodium nitrite, the oil was assumed to be pure *m*-bromo-dimethyl-aniline.

[2] Lieberman's nitrosamine test.

[3] Wurster also gave 148° as the melting-point of the compound.

with hydrochloric acid to the consistency of a thick paste, added to it in small portions. The reduction was practically instantaneous. The complex tin salt of the dihydrochloride of the $m$-bromo-dimethyl-$p$-phenylene-diamine separated. Enough water was then added to bring it back into solution, and the tin precipitated as stannic sulfide from the hot solution with hydrogen sulfide. Before being filtered the solution was diluted with an equal amount of water, warmed to 80°, and hydrogen sulfide passed through it for a half an hour longer. This procedure has been found very satisfactory, requiring very little time and precipitating the tin quantitatively in one operation. The water in the filtrate was distilled off *in vacuo*. The dihydrochloride of $m$-bromo-dimethyl-$p$-phenylene-diamine remained behind. It was purified by preparation of the free base and distillation of the latter *in vacuo*. The base was then dissolved in ether and dry hydrogen chloride passed into the solution. The dihydrochloride was precipitated. It was dried in a vacuum desiccator.

Subs., 0.1941: 16.80 cc. dry $N_2$ at 20° and 726.3 mm.
Calc. for $C_8H_{10}N_2Br.2HCl$: N, 9.81. Found: 9.64.

$m$-**Bromo-dimethyl-$p$-phenylene-diamine,** $BrNH_2C_6H_3N(CH_3)_2$.—The free base was obtained by the method previously outlined. The oily distillate solidified on cooling in white, almost colorless, needles; m. p. 47.5°. The free base turned dark on exposure to light and air. When it was dissolved in dil. hydrochloric acid and the solution was saturated with hydrogen sulfide and treated with ferric chloride, an intensely blue coloration was produced.

Subs., 0.2749: AgBr, 0.2406.
Calc. for $C_8H_{11}N_2Br$: Br, 37.18. Found: 37.25.

$o$-**Dibromo-Bindschedler's Green.**—The same method was employed as was used originally by Bindschedler for the preparation of Bindschedler's Green.[1] To a mixture of 2.15 g. of $m$-bromo-dimethyl-$p$-phenylene-diamine and 2 g. of $m$-bromo-dimethyl-aniline,[2] 2 g. of conc. hydrochloric acid in 50 cc. of water was added. The solution was cooled to —2° and oxidized by a solution of 2 g. of potassium dichromate and 0.6 g. of glacial acetic acid in 20 cc. of water. The oxidizing agent was added drop by drop. The flask was shaken continuously during the addition of the oxidizing agent. The dyestuff partly precipitated out. Sufficient water was then added to redissolve it, the solution heated to 40–50° and 5 g. of zinc chloride added to it. It was allowed to stand in ice-water for 2 hours longer and the precipitate collected on a filter, washed with a small quantity of cold water, then with alcohol, and finally with ether. It was dried in a vacuum desiccator. A dark amorphous powder was

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[1] Bindschedler, *Ber.*, **16**, 864 (1883).
[2] Prepared by the method of Wurster, *ibid.*, **16**, 864 (1883).

thus obtained which was slightly soluble in water, imparting to the latter an intensely green color. The yield was very good.

Subs., 0.3618: 27.40 cc. dry $N_2$ at 24.5° and 731 mm.

Subs., 0.4860: ZnO, 0.0382.

Calc. for $C_{32}H_{36}N_6Br_4Cl_2.ZnCl_2$: N, 8.25; Zn, 6.37. Found: N, 8.36; Zn, 6.31.

The analysis readily shows that in this case also 2 molecules of the dye combine with one of zinc chloride.

The mercuric chloride double salt was obtained by solution of the zinc chloride double salt in water at 40–50°, and addition of mercuric chloride. The structure of the compound thus obtained is expressed by the following formula,
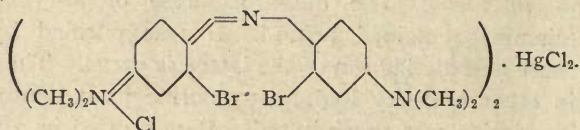


Subs., 0.1373: HgS, 0.0278.

Calc. for $C_{32}H_{36}Br_4Cl_2.HgCl_2$: Hg, 17.17. Found: 17.47.

Work is also under way on the isolation of the leuco-dibromo-Bindschedler's Green, and the replacing in the latter of the 2 bromine atoms by mercury to give a compound of the following type,
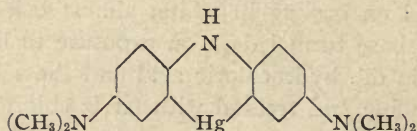


which, when oxidized, would give a representative of a new class of organic mercury derivatives.

*m* - **Bromo** - **phenylmethyl** - **nitrosamine**, $m$-$BrC_6H_4N(CH_3NO)$.—As previously stated, the methylation of *m*-bromo-aniline by the use of dimethyl sulfate gave rise to 2 derivatives, the mono-methyl and the dimethyl *m*-bromo-anilines. These 2 were separated by the use of sodium nitrite as given in detail in the preparation of *p*-nitroso-*m*-bromo-dimethylaniline. The ether extract of the acid solution contained the *m*-bromomethylphenyl-nitrosamine. The ether was distilled off and the oil subjected to steam distillation. The distillate was then extracted with ether, the solution dried with sodium sulfate, and the ether distilled off. When the sides of the crystallizing dish were cooled and scratched the oil solidified in feathery clusters of fine yellowish needles; m. p., 49°. Yield, 10 g.

Subs., 0.2049: AgBr, 0.1782.

Calc. for $C_7H_7ON_2Br$: Br, 37.17. Found: Br, 37.01.

The compound gives the characteristic Lieberman's nitroso-amine reaction and in the pure condition is very stable.

**p-Nitroso-*m*-bromo-monomethylaniline,** $BrNOC_6H_3NHCH_3$. — The *m*-bromo-methylphenyl-nitrosamine was rearranged according to the method of Fisher and Hepp.[1] The nitrosamine (4 g.) was dissolved in ether (8 g.) and alcohol (16 g.), saturated with hydrogen chloride at 10°, added. A red coloration was produced after the addition of the alcohol. It took fully 2 days for the reaction to go to completion. A beautiful pink compound was obtained. This compound, the hydrochloride of *p*-nitroso-*m*-bromo-monomethyl-aniline, is very stable, much more so than the hydrochloride of the dimethyl-aniline derivative. It was kept 3 weeks in an open dish without changing color. Its melting-point was not sharp. At 140° it turned yellow, and at 168° melted with apparent decomposition. It hydrolyzed immediately to give the free base on suspension in water. The free base was isolated and purified by the same method as that given for *p*-nitroso-*m*-bromo-dimethyl-aniline.

> Subs., 0.1055: 12.11 cc. dry $N_2$ at 20 and 736 mm.
> Calc. for $C_7H_7ON_2Br$: N, 13.06. Found: 12.95.

The free base is green. It has no definite melting-point. It turns dark at 100° and explodes at 124°. An ether solution of the base is yellowish-green in thin layers and green in thick.

**p - Nitroso - phenol - *o* - mercuric - chloride,** $HOC_6H_3(4)NO(2)HgCl$.— Three g. of *o*-phenol-mercuric chloride was gradually added to a solution of 0.42 g. of sodium hydroxide and 0.86 g. of sodium nitrite in 23 cc. of water. The solution was warmed to 30–40° and a few drops of 2 molar sodium hydroxide solution added to it until all of the *o*-phenol-mercuric-chloride had gone into solution. When finely powdered, it goes into solution rapidly in the given amount of sodium hydroxide.[2] It was cooled to —4° or —5° and 2.3 g. of conc. sulfuric acid in 6 cc. of water added very slowly. The flask was constantly shaken during the operation. The addition of the acid should take about 45 minutes. The solution first turned pink, due to the formation of the sodium salt of the *p*-nitroso-phenol-*o*-mercuric chloride, but it grew darker and darker in color as more of the acid was added. A dark-colored precipitate was also formed. After all the acid had been added, the solution was shaken for 15 minutes longer, and allowed to stand in a freezing mixture for 2 hours to complete the precipitation. The solution was then filtered and the residue, after being washed a few times with small amounts of cold water, dried in a vacuum desiccator over solid sodium hydroxide and soda lime. A beautiful bordeaux-colored compound was thus obtained which can be kept indefinitely over soda lime without decomposition. It can be recrystallized

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[1] Fisher and Hepp, *Ber.*, **19**, 2991 (1886).

[2] It has also been found very advantageous to moisten the *o*-phenol-mercuric-chloride with a few drops of alcohol. It then dissolves in the alkali very readily—for very obvious reasons.

from xylene in which it is slightly soluble and also from anisol from which it separates in very small needles of a light brown color.

> Subs., 0.1930: 6.72 cc. dry $N_2$ at 22° and 732.3 mm.
> Subs., 0.1352: AgCl, 0.0547.
> Calc. for $C_6H_4O_2NClHg$: N, 3.92; Cl, 9.92. Found: N, 3.90; Cl, 10.07.

The compound, like $p$-nitroso-phenol, gives the Lieberman's nitrosamine test. It is partly soluble in ether, imparting to the latter an intensely green color. It behaves in all respects except solubility, like $p$-nitroso-phenol, of which it is a substituted derivative as noticed from the method of preparation. The mercury in *ortho* position to the hydroxyl group in phenol is known not to decrease the activity of the *para* hydrogen atom, as illustrated by the fact that it is possible to couple $o$-phenol-mercuric-chloride with diazo compounds.[1]

**$p$-Nitroso-aniline-$o$-mercuric-chloride,** $NH_2C_6H_3(4)NO(2)HgCl$.—To 2 g. of $p$-nitroso-phenol-$o$-mercuric-chloride, 2.4 g. of ammonium chloride, 6.6 g. of dry ammonium acetate, and 0.2 g. of ammonium carbonate were added and the mixture warmed on the water-bath for $1/2$ hour with vigorous stirring.[2] It was then poured into 75 cc. of cold water, and allowed to stand $1/2$ hour. A slightly brown amorphous precipitate was obtained. It was filtered off, washed well with cold water until the washings gave no test for ammonia to Nessler's reagent and dried in a vacuum desiccator over sodium hydroxide. For purification, it was recrystallized from anisol.

> Subs., 0.1431, 0.1311: (1) 9.80 cc. dry $N_2$ at 23° and 729.5 mm., (2) 8.90 cc. dry $N_2$ at 19° and 739.5 mm.
> Subs., 0.1248: AgCl, 0.0530.
> Subs., 0.1252: HgS, 0.0823.
> Calc. for $C_6H_5ON_2ClHg$: N, 7.89; Cl, 9.98; Hg, 56.31. Found: N, 7.53; Cl, 10.18; Hg, 56.57.

The compound is slightly soluble in benzene and ether, coloring both green. An alcohol solution is reddish-yellow.

In the preparation of the above compound, smaller or larger quantities of the $p$-nitroso-phenol-$o$-mercuric-chloride sometimes remain unchanged. So it is always advisable to test the $p$-nitroso-aniline-$o$-mercuric-chloride by the Lieberman's nitrosoamine reaction for its presence. If the test is positive, the precipitate must be washed by decantation with a 2 molar solution of sodium hydroxide until the washings are colorless—the phenol derivative being soluble. It is then washed free from alkali with cold water and dried in a vacuum desiccator over sodium hydroxide.

**Diphenylamino - tetramercuric - chloride,** $HN\left(\!-\!\langle\!\bigcirc\!\rangle\!-\!HgCl\right)_2$ .—Di-

HgCl

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[1] Dimroth, *Centr.*, **1901**, I, 450.
[2] Fisher and Hepp, *Ber.*, **20**, 2475 (1887).

phenylamine (6.5 g.) was heated with mercuric chloride (2.7 g.) until the latter seemed to go into solution. A crackling noise was heard and the reaction went on of its own accord with the evolution of heat. The solution was first yellow, then brown, and finally dark brown. It was then poured into glacial acetic acid and boiled. The acid was decanted. The washing with glacial acetic acid was continued until the decanted liquid poured into water gave no precipitate, indicating that the product was free from diphenylamine. The filtrate was tested for mercuric chloride until the precipitate was washed free from it. A light yellow amorphous compound was thus obtained as a residue which, after being boiled with alcohol, was dried in a vacuum desiccator.

Subs., 0.8889: 10.20 cc. of $N_2$ at 21° and 734.2 mm.
Subs., 0.1940: AgCl, 0.1012.
Subs., 0.1699: HgS, 0.1426.
Calc. for $C_{12}H_7NCl_4Hg_4$: N, 1.26; Cl, 12.81; Hg, 72.26. Found: N, 1.28; Cl, 12.98; Hg, 72.10.

The compound is insoluble in all organic solvents. It does not melt when heated to 260°. When boiled with pyridine, it seems to undergo decomposition. This is probably a ring formation as large quantities of mercuric chloride are found in the pyridine. It is being investigated. From consideration of analogous cases the positions taken by the mercury are most likely *para* and *ortho* to the nitrogen. Thus, *p*-toluidine yields a mono-substitued derivative when treated with mercuric acetate or chloride, *o*-toluidine a di-substituted derivative, and *m*-toluidine a tri-substituted derivative. In these compounds mercury occupies the positions, relative to the nitrogen, *p*, *p-o*, *p-o-o*, respectively. Furthermore, the literature is abundant with instances of similar substitutions. In no case, however, has a mercury compound been prepared in which mercury would occupy a position *meta* to an amino nitrogen. We feel, therefore, in some way justified in assigning the above structure to the diphenylamine derivative.

### 3,3'-Mercuri-mercazine,
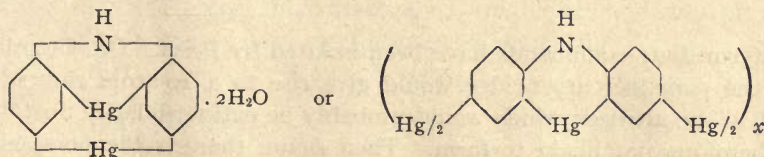


To 5 g. of diphenylamine-tetramercuric-chloride in 60 cc. of alcohol was added 10 g. of sodium thiosulfate in a little water. The precipitate turned dark immediately. The solution was warmed to 70° and kept at that temperature for 15 minutes, the whole being shaken during the operation. Sufficient water was then added to get a homogeneous solution, the solution boiled a few minutes and then filtered. The precipi-

tate was washed with alcohol and then with ether, dried and then analyzed.

Subs., 0.1949: 4.60 cc. of dry $N_2$ at 21° and 730.2 mm.

Subs., 0.1478: HgS, 0.1142.

Subs., 0.3082: $CO_2$, 0.2739; $H_2O$, 2.09.

Subs., 0.2133: AgCl, 0.0008.

Calc. for $C_{12}H_{11}ONHg_2$: N, 2.33; C, 23.97; H, 1.83; Hg, 66.50. Found: N, 2.53; C, 24.22; H, 2.09; Hg, 66.60.

The compound is of a gray color, resembling finely precipitated metallic mercury. It is insoluble in all organic solvents. When heated to 100° in a vacuum, mercury distils over. The substance is unstable when treated with nitric acid. The product of nitration is soluble in sodium hydroxide with a red coloration.

The structural formula of this compound is of great interest. The structure which suggests itself from the method of preparation is,
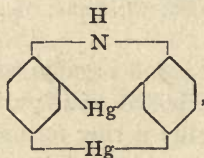


since from the work of Pesci[1] on aniline mercuri-acetate and similar compounds it is quite evident that the sodium thiosulfate acts in the following way
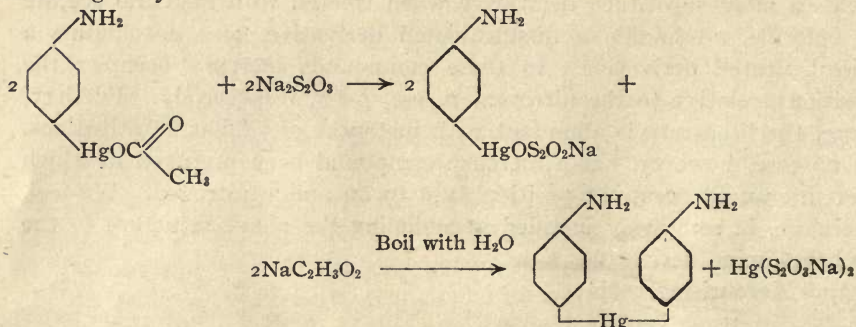


The intermediate compounds have been isolated by Pesci. On the other hand, the *para* mercury bridge would give rise to a 10-atom ring with respect to the nitrogen which would probably be extraordinarily unstable and, therefore, not likely to form. Then again, there is the possibility of the formation of a complex molecule of the type
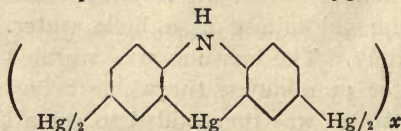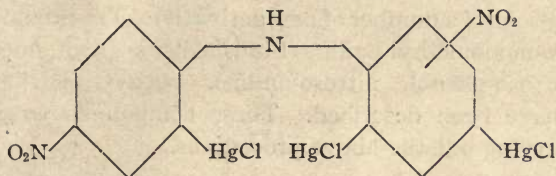


[1] Pesci, *Gazz. chim. ital.*, **29**, I, 394 (1899).

We have not been able so far, however; to confirm either assumption, owing to the insolubility of the compound in all solvents.

### $p,o,o'$-3-Mercuric-chloride-di-nitro(??)diphenylamine,



To 5 g. of diphenylamine-tetramercuric-chloride 20 g. of a mixture of conc. nitric acid (2 parts sp. gr. 1.4), sulfuric acid (1 part), and water (one part) were added. It was warmed carefully for 2 minutes. The nitration took place with vigor. When the reaction had completed itself, the contents were poured into water, boiled, and the solution filtered. The residue was washed with alcohol and ether and dried in a vacuum desiccator.

Subs., 0.2491, 0.1732: (1) 10.00 cc. of dry $N_2$ at 20° and 728 mm.; (2) 6.60 cc. of dry $N_2$ at 21° and 740 mm.

Subs., 0.2518: $CO_2$, 0.1532; $H_2O$, 0.0159.

Subs., 0.2000: AgCl, 0.0900.

Subs., 0.1320, 0.1831: (1) HgS, 0.0954; (2) 0.1328.

Calc. for $C_{12}H_6O_4N_3Cl_3Hg_3$: N, 4.39; C, 14.93; H, 0.63; Cl, 11.03; Hg, 62.24. Found: N, 4.29; C, 14.72; H, 0.70; Cl, 11.13; Hg, 62.52.

The compound is of a light brown color. It is insoluble in all organic solvents. It is partly soluble in sodium hydroxide, giving the solution a red coloration.

### Mercury-bis-3-di-nitro(?)-mercazine,
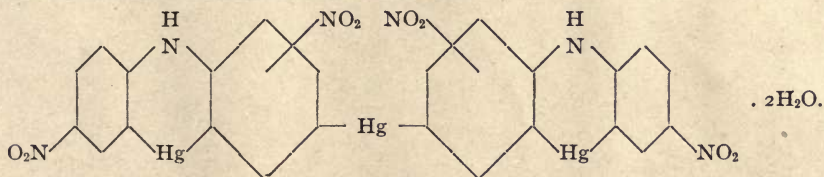


Starting with the above nitro compound, this compound was prepared by the same method as used for 3,3'-mercuri-mercazine.

Subs., 0.2248: 14.20 cc. of dry $N_2$ at 20° and 738.7 mm.

Subs., 0.1384: $CO_2$, 0.1218; H.

Subs., 0.1101: HgS, 0.0642.

Calc. for $C_{24}H_{10}O_{10}N_6Hg_3$: N, 7.09; C, 24.24; H, 1.52; Hg, 50.54. Found: N, 7.16; C, 24.01; H, 1.98; Hg, 50.26.

The compound is of a light brown color. It is insoluble in all organic solvents. When treated with sodium hydroxide, it gives to the latter a light red coloration. It resembles the other mercazine derivative in many respects. When heated in a vacuum to 100°, it loses mercury. Heated to 54° in a vacuum for fifteen minutes, it loses 5.22% of water.

## Conclusions.

1. A few methods have been outlined for the preparation of a 6-atom heterocyclic ring containing mercury in place of a non-metal.

2. The preparations of a number of new derivatives of *m*-bromo-dimethyl-aniline, *m*-bromo-monomethyl-aniline Bindshedler's green, mercury derivatives of nitroso-phenol, nitroso-aniline, phenylamine and nitro-diphenylamine have been described. These compounds were obtained as a result of carrying out the above procedures.
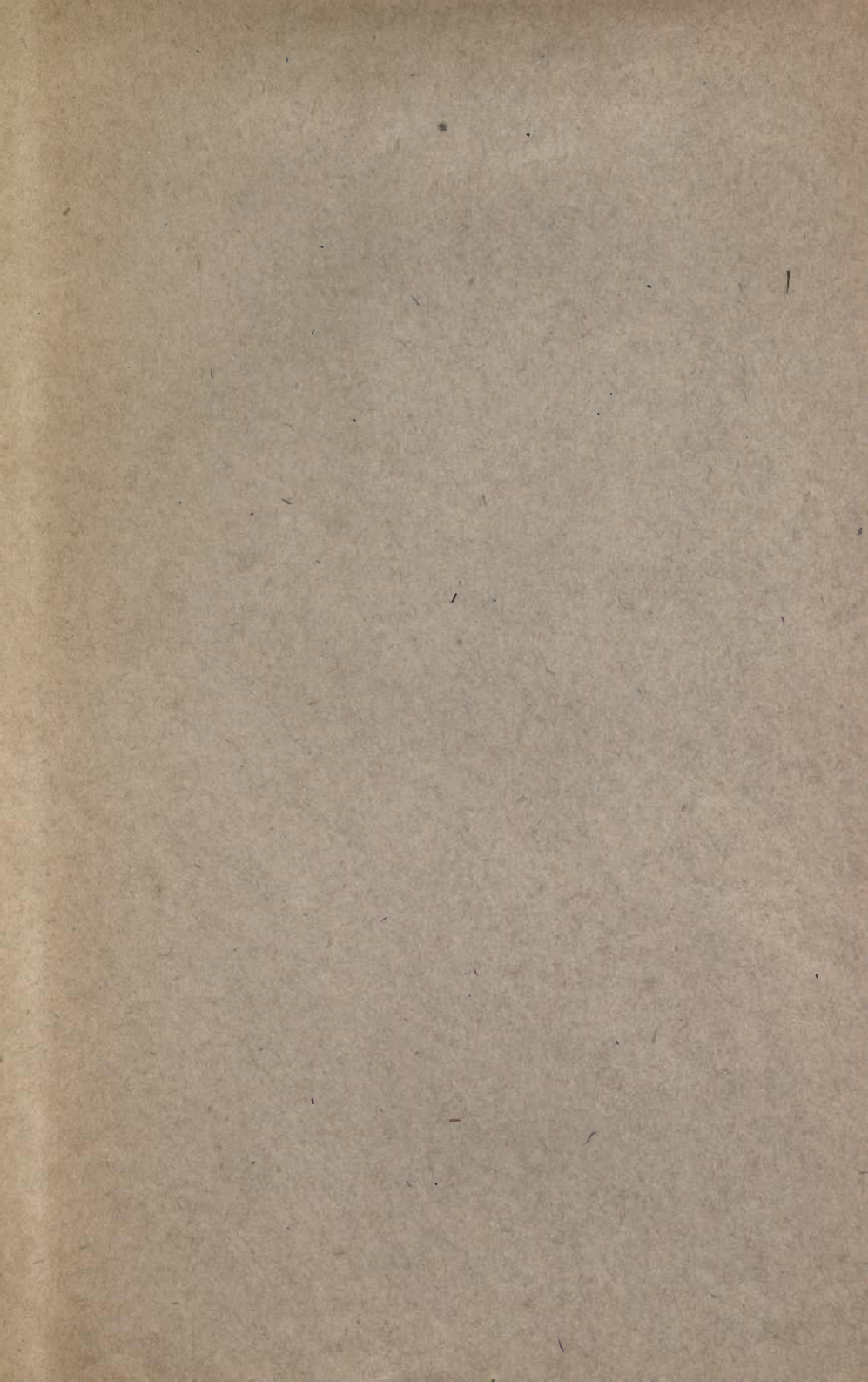
In conclusion, the writer takes pleasure in acknowledging gratefully his appreciation of Dr. Piccard's guidance, encouragement and personal kindness in the course of this work.